# LINEAR RHEOLOGY OF BINARY MELTS FROM A PHENOMENOLOGICAL TUBE MODEL OF ENTANGLED POLYMERS

**Amalie L. Frischknecht**[a] and **Scott T. Milner**[b]

[a]Sandia National Laboratories
PO Box 5800, MS-1411
Albuquerque, New Mexico 87185-1411
alfrisc@sandia.gov

[b]ExxonMobil Research and Engineering Co.
Annandale, New Jersey 08801
scott.t.milner@exxonmobil.com

We develop a simple phenomenological theory to describe linear viscoelasticity in bidisperse linear polymer melts. The dynamics of linear entangled polymers are well described by tube models, in which the primary motion of the chains is reptation, curvilinear diffusion along a tube formed by entanglements with other chains. However, to be in agreement with experiment, contour-length fluctuations and constraint-release effects must also be included. These effects are particularly important to include in any theory of the viscoelastic response of polydisperse melts, since shorter chains relax more quickly than longer ones, and will thus release some of the constraints on long chains before the long chains relax by reptation.

The goal of this work is to develop a simple approximation to the calculation of the relaxation modulus for entangled binary melts which nevertheless captures the essential features of the release of constraints due to contour-length fluctuations. We develop a phenomenological single-chain relaxation spectrum, in which the relaxation time $\tau(s)$ of each tube segment locally along the chain depends on its distance $s$ from the free end. We incorporate both contour-length fluctuations and reptative motion in the single-chain relaxation. The effects of constraint release are taken into account in the complex modulus using the idea of dynamic dilution, by summing the contributions from all the segments along the chain, and weighting the contributions by the entangled volume fraction remaining at each time $\tau(s)$. The model involves two universal constants which are determined by comparison to the more complete theory of Milner and McLeish [1] for monodisperse polymer melts. The two remaining adjustable parameters, the relaxation time $\tau_e$ of an entanglement segment and the plateau modulus $G_N^0$, are the same as in other theories and are obtained by fits to the data for the monodisperse melts comprising a given binary blend. We find that the resulting predictions for the complex modulus fit data on binary blends of polybutadiene much better than does the widely-used double reptation model.

**References**

[1] S. T. Milner and T. C. B. McLeish, "Reptation and contour-length fluctuations in melts of linear polymers," *Phys. Rev. Lett.*, v. 81, p. 725–728, 1998.